

RAW MATERIALS

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PROPERTIES OF CLAYS FOR MANUFACTURING SANITARY WARE

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Clays from different producers are investigated. The chemical and mineral compositions and the granularity of the clays are analyzed. Their basic differences and the effect on the properties of the finished pastes are shown. The clay properties which are necessary to optimize the composition of ceramic pastes are determined. The rheological characteristics and how they affect the control of the technological process are examined. The main advantages and disadvantages of different clays — traditional domestic clays and some new ones — are established.

One of the most complex processes in the technology of ceramics is forming the intermediate product by casting in a plaster-of-Paris mold. The crucial state in this process is preparing the casting slip, whose properties largely determine the molding time and the quality of the intermediate and finished products.

Clays and kaolins are the principal raw materials, which are components of slips and have a large effect on their technological properties, for manufacturing sanitary ware. Clay materials give ceramic paste plasticity, i.e., the necessary molding properties; they impart strength to the dried intermediate product and, being the main source of mullite formation, they increase the thermal and chemical resistance of the calcined articles. The suitability of clays for manufacturing ceramic articles is determined by a complex of physical-technical properties of clay (molding, drying, and calcining), which are determined by its plasticity, the liquescence imparted to suspensions by electrolytes, the sensitivity to drying, baking, phase changes and transformations which clays undergo during calcination, and other properties. In turn, the above-listed properties of clays are predetermined by their mineral composition, the size range and morphology of the clay particles, and the impurity composition [1].

Our work is devoted to studying and comparing the properties of clays obtained from different deposits. The Russian clays Baranovskoe (B-0), Shulepovskoe (Sh-1), and Latnenskoe (LT), the Ukrainian clay "Vesko," which is typical for clays produced in the Druzhkov Basin and tradition-

ally used by Russian manufacturers, and a new product on the Russian market — the English clay SanBlend 75 (SN-75) produced by the WBB company and widely used by European manufacturers of sanitary ware — were analyzed.

The chemical composition of the clay raw material is one of the main indicators used when selecting a component of the final mixture. The most important constituent of clays is alumina Al_2O_3 , which has the largest effect on the properties of ceramic articles. As the Al_2O_3 content increases, the refractoriness and mechanical strength of the materials increase. On the one hand SiO_2 in substantial quantities decreases the plasticity of ceramic paste and the shrinkage (it improves the conditions for drying and calcining), but on the other hand it decreases refractoriness.

The content of the coloring oxides — iron and titanium oxides — must satisfy the most stringent requirements. When excess iron and titanium oxides are present, the porcelain or delftware acquires a red, brown, yellow, and light-violet color; manganese oxides impart orange and black colors. In addition, iron and titanium oxides are strong fluxes, which decrease the viscosity of the liquid phase and the calcination time as well as the mechanical strength of the articles. Calcium oxide, which is often encountered in kaolins, serves as a flux. The negative effect of this oxide is also manifested in degradation of the structural-mechanical properties of clays, specifically, greater rippling and decreased fluidity and liquescence of the slip [2].

The presence of water-soluble salts, especially calcium, magnesium, or iron sulfates but also chloride salts, in clays and kaolins decreases the liquescence power of water glass.

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TABLE 1

Clay	Mass content, %								Concentration, mg/kg				
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	calcination loss	Ca ²⁺	Mg ²⁺	chlorides	sulfates
“Vesko”	59.93	28.26	0.99	1.28	0.45	0.49	1.91	0.62	8.08	64.0	25.0	163.0	243.0
LT-T	55.63	30.34	0.87	1.63	0.38	0.27	0.29	0.07	10.51	8.7	3.0	10.0	50.0
Sh-1	50.11	33.03	2.11	1.02	0.48	0.30	0.80	0.12	12.03	114.0	18.0	12.0	50.0
B-0	47.87	34.12	2.02	1.72	0.32	0.20	0.18	0.07	17.50	296.0	84.0	10.0	1040.0
SN-75	53.73	28.81	1.10	1.22	0.20	0.30	2.33	0.32	12.11	2.5	1.0	—	—

Mechanical impurities, mainly, free silica sand, in the form of quite large grains and impurity residues of undecomposed rocks, greatly decrease the plasticity of the ceramic paste. In addition, large impurity particles destroy the homogeneity of the paste and increase its sintering temperature and crack formation.

We shall examine some of our data on the clay compositions studied. The chemical composition was analyzed by x-ray fluorescence analysis (the Philips system). In addition, solutions of kaolins (solid : water = 1 : 10) were prepared and the content of the soluble salts as well as the presence of sulfates and chlorides were checked. The results are presented in Table 1. The clays tested differ substantially with respect to chemical composition. The B-0, Sh-1, and LT-T clays have a high Al₂O₃ content (30 – 34%). The “Vesko” and SN-75 clays are characterized by a lower content of Al₂O₃ (28%) and are distinguished by a high content of K₂O and Na₂O. The B-0 and Sh-1 clays have the highest content of coloring oxides. Investigations of the eluates showed that the “Vesko” and B-0 clays exhibit the highest contamination with soluble salts. Few impurities are present in SN-75 clay; this is its main difference from the other clays. The high content of coagulant ions in the clays will sharply increase the viscosity of the finished slip and, in consequence, the content of electrolytes in the paste.

Aside from the chemical composition, especially of clays and kaolins, it is important to know the phase composition of the minerals in order to devise the composition of the ceramic paste. The mineral composition of the clay raw material is one of the main indicators determining the salient features of its structure formation and properties. Kaolinite, montmorillonite, and hydromica are the principal clay-forming minerals. They are primarily hydrous alumina silicates, containing silica and iron oxides as well as sulfates, carbonates, and water-soluble salts of various minerals with particle size less than 5 μm . As a rule, refractory clays are monomineral and low-melting clays polymineral substances. Kaolinite clays are distinguished by the following: they swell very little in water and they are essentially nonreactive to acids. Montmorillonite clays swell strongly in water and are very plastic. Clays containing only montmorillonite minerals are called bentonite. Hydromicaceous clays possess average

plasticity. Quartz, limestone, and dolomite are the mineral impurities most often encountered in clays [3].

X-ray diffractometry was used to analyze the mineral composition of the clays. The results are presented in Table 2. The principal mineral in the B-0, Sh-1, LT-T, and SN-75 clays is kaolinite (76 – 86%). These clays are observed to have a negligible quartz content — 7 – 14% (the quartz content is higher in LT-T clay — 20%) and a small amount of three-layer minerals (2 – 8%) and admixtures of mica (2.0 – 3.5%). It should be noted that there are virtually no three-layer minerals in the SN-75 clay. The “Vesko” clay contains, besides kaolinite (45%), a high relative fraction of quartz (26%) and three-layer clay minerals (25%), which are capable of partial swelling.

Clay rocks consist of particles of different size. Thin clay fractions with grain size less than 0.5 – 1.0 μm increase the reactivity of clays during calcination and other processes. The clay particles are very small and have a plate structure, as a result of which they can abut one another. This gives rise to the most important property of clays — their impermeability to water. Another important property of clays is closely related to this — plasticity, i.e., the capability to assume and hold prescribed shapes. Clays also contain dust-like fractions (with grain sizes 5 – 50 μm) and sandy fractions (from 50 μm to 3 mm). The granularity of different types of kaolins can be different [4].

A sedimentation analysis was performed with a Sedigraph 5100 to determine the granularity of kaolins. It was determined (see Fig. 1) that the clays B-0 and “Vesko” have the smallest grains. The clays Sh-1 and LT-T follow. The clay

TABLE 2

Minerals	Mass content, %, in clay				
	“Vesko”	LT-T	Sh-1	B-0	SN-75
Feldspars	1.7	1.0	1.3	1.5	1.7
Quartz	26.0	20.0	11.0	7.0	14.0
Three-layer clay minerals	25.0	3.0	8.0	2.0	0.5
Kaolinite	45.0	74.0	76.0	86.0	81.3
Mica	2.3	2.0	3.7	3.5	2.5

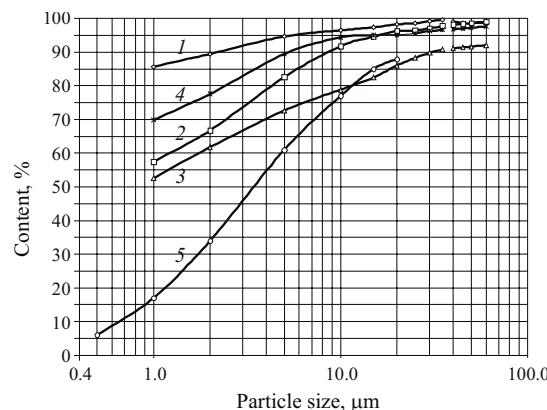


Fig. 1. Granularity of the clays B-0 (1), Sh-1 (2), LT-T (3), "Vesko" (4), and SN-75 (5).

SN-75 has a completely different composition and is characterized by a low content of fractions up to 1 μm ; the quantity of coarse fractions is also small. Thus, the principal distin-

TABLE 3

Quantity of electrolyte in the clay, %	Galencamp rotation angle, deg			Hardening time, min	Thickness of the body gathered in 60 min, mm
	immediately after	after 10 min	difference		
"Vesko" clay					
1.000	130	-80	210	> 120	3.2
1.050	260	150	110	55	2.3
1.100	282	202	80	40	2.0
1.150	294	253	41	25	1.9
1.200	310	287	23	20	1.7
1.300	272	252	20	15	1.8
B-0 clay					
1.450	-20	-	-	-	-
1.500	330	250	80	75	4.6
1.550	329	288	41	10	3.2
1.575	347	342	5	10	2.9
1.600	343	333	10	10	3.4
Sh-1 clay					
0.250	347	315	32	9	3.9
0.275	350	335	15	8	3.7
0.300	350	350	0	7	3.4
0.350	345	338	7	8	3.3
LT-T clay					
0.175	339	298	41	9	3.9
0.200	345	322	23	8	3.5
0.250	345	333	12	8	3.5
0.300	357	350	7	7	3.3
SN-75 clay					
0.150	340	314	26	8	5.5
0.175	350	345	5	7	5.4
0.200	350	347	3	7	4.9
0.250	357	357	0	6	4.9

guishing feature of SN-75 clay is a narrow particle-size range — mainly from 1 to 10 μm .

The most important property of clays for manufacturing articles by casting is their liquescence, as a result of which their moisture content decreases and adequate mobility of the slip is maintained when filling molds, which is accomplished by introducing liquefying electrolytes into the slip. These electrolytes interact with the suspension, which has the principal properties of colloidal systems and the capability of entering exchange interactions and sorbing water.

Plastic materials have a large effect on the rheological properties of the casting slip. Measurements of the rheological characteristics of a suspension are the final assessments in determining the physical and chemical properties of the clay raw material. These measurements make it possible to predict the properties of the slip and can be used to control the technological slip-preparation process.

Batches consisting of 500 g of dry solid material were used to investigate liquescence. The slip was allowed to stand for at least 16 h before the tests were performed. The tests were performed with a Galencamp coaxial-cylinder viscosimeter. The angle of rotation was measured immediately and 10 min after the slip was poured.

The following properties were investigated separately: density, viscosity and thixotropy following Galencamp, casting formation, hardening time (filtration properties), stability and properties when removing the casting from the mold. The results obtained are presented in Table 3.

Obviously, the composition of clays also affects the rheological properties of slip. The SN-75 clay requires the smallest amount of electrolyte. The LT-T and Sh-1 clays follow. The SN-75 clay exhibits the best casting formation and filtration behavior. The LT-T and Sh-1 clays also show satisfactory results. The "Vesko" and B-0 clays require a much larger amount of electrolyte; they form only a thin casting layer.

The thickness of the gathered body is largest for "Vesko" clay with 1% electrolyte content — 3.2 mm. The hardening time in this case was longer than 120 min. The mass is easily removed from the mold and does not stick to the wall. The maximum thickness of the gathered body for B-0 clay (4.6 mm) corresponds to the lowest content of electrolyte (1.5%). The surface of the casting is rippled and the cast is difficult to remove from the mold. For Sh-1 clay with different electrolyte content, the hardening time is stable (7–9 min). The maximum thickness of the gathered layer is 3.9 mm with electrolyte content 0.25%. The clay forms a casting with an even surface; the casting is easily removed from the mold and does not stick to its walls.

The LT-T and Sh-1 clays have similar rheological properties. The maximum thickness of the gathered body, equal to 2.9 mm, corresponds to a lower electrolyte content (0.175%) than for Sh-1 clay.

The SN-75 clay is characterized by the largest thickness of the gathered body with the lowest electrolyte content

TABLE 4

Clay	Flexural strength after drying, MPa	Shrinkage, %			Water absorption, %
		air	calcination*	total	
“Vesko”	6.0	9.9	8.7	17.6	0.53
B-0	3.0	4.0	14.9	18.3	1.53
Sh-1	2.9	3.8	9.9	13.2	5.46
LT-T	2.5	5.5	8.6	13.7	6.50
SN-75	3.5	3.8	12.0	15.8	0.48

* After calcination at 1220°C.

(0.15%) of all the clays analyzed. The clay possesses good casting properties; the casting has a uniform thickness and is easily removed from the mold.

To optimize the composition of the ceramic paste it is important to determine the physical properties of the green (after drying) and the ceramic properties of the calcined samples of the raw materials. The flexural strength and shrinkage after drying were measured for samples of kaolins which had not been calcined. Test rods were cast for this purpose. After the samples were calcined (maximum temperature 1220°C) the deformation, shrinkage during calcination, and water absorption were measured. The results are presented in Table 4. As far as the ceramic properties are concerned, “Vesko” clay exhibits the highest shrinkage on drying and the highest flexural strength. The “Vesko” and SN-75 clays have the lowest water absorption after calcination, which indicates that their sinterability is good. The B-0 clay shows the greatest total shrinkage and shrinkage on calcination. After calcination, this clay has a structured (cellular) surface. The Sh-1 and LT-T clays have the same ceramic properties. They are characterized by the highest water absorption after calcination.

Investigating different properties of raw materials makes it possible to optimize the composition of the paste in order to solve technological problems and ensure the highest performance of equipment. Most of the clays studied can be

used to optimize the formulas for the paste used to manufacture sanitary ware.

The B-0 clay cannot be used for sanitary ware. This clay has the highest content of coloring oxides and soluble salts, as a result of which its liquescence is poor. The “Vesko” clay has poor liquescence; this clay is distinguished by a high plasticity but also a normal tendency to sinter. Such a raw material is also suboptimal for ceramic pastes to be used for casting. This clay can be used in small quantities as an additive to coarsely dispersed clay of higher quality.

The LT-T and Sh-1 clays are more acceptable for casting slips. As a result of the low sinterability of these clays, additional amounts of feldspar must be added to the pastes for the ceramic to sinter completely.

The SN-75 clay is best for manufacturing sanitary ware and meets the highest standards for high-technology production. The WBB Company uses a multistep system of enrichment to obtain the clays, including wet enrichment, which makes it possible to attain stable parameters with respect different properties. However, the high cost of SN-75 clay will have a large effect on the production costs, which ultimately can affect the competitiveness of the final product.

The ceramic industry cannot advance if manufacturers are not given high-quality raw materials which make it possible to develop new technologies and to manufacture more complex articles of high quality with the required productivity of labor.

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